

FORM PTO-1390 (Modified)
(REV 11-2000)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES

DESIGNATED/ELECTED OFFICE (DO/EO/US)

CONCERNING A FILING UNDER 35 U.S.C. 371

209442US0PCT

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

09 / 857210

INTERNATIONAL APPLICATION NO.

PCT/EP99/10112

INTERNATIONAL FILING DATE

20 December 1999

PRIORITY DATE CLAIMED

24 December 1998

TITLE OF INVENTION

METHOD FOR PRODUCING AN ULTRAPHOBIC SURFACE BY SANDBLASTING

APPLICANT(S) FOR DO/EO/US

Karsten REIHS, et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☒ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☒ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A copy of the International Search Report (PCT/ISA/210).

Items 13 to 20 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☐ Certificate of Mailing by Express Mail
23. ☒ Other items or information:

PCT/IB/304

Notice of Priority

Request for Consideration of Documents Cited in International Search Report

| | | | | | |
|--|--|---|--|--|--|
| U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.53) <div style="font-size: 24pt; font-weight: bold;">09/857210</div> | | INTERNATIONAL APPLICATION NO. <div style="font-weight: bold;">PCT/EP99/10112</div> | | ATTORNEY'S DOCKET NUMBER <div style="font-weight: bold;">209442US0PCT</div> | |
|--|--|---|--|--|--|

24. The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :

- ☐ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1000.00
- ☒ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$860.00
- ☐ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00
- ☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00
- ☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00

ENTER APPROPRIATE BASIC FEE AMOUNT =

Surcharge of **\$130.00** for furnishing the oath or declaration later than ☐ 20 ☒ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)). **\$130.00**

| CLAIMS | NUMBER FILED | NUMBER EXTRA | RATE | | |
|---|--------------|--------------|-----------|--|--------------------------|
| Total claims | 19 - 20 = | 0 | x \$18.00 | | \$0.00 |
| Independent claims | 1 - 3 = | 0 | x \$80.00 | | \$0.00 |
| Multiple Dependent Claims (check if applicable). <input type="checkbox"/> | | | | | \$0.00 |
| TOTAL OF ABOVE CALCULATIONS = | | | | | \$990.00 |
| <input type="checkbox"/> Applicant claims small entity status. (See 37 CFR 1.27). The fees indicated above are reduced by 1/2. | | | | | \$0.00 |
| SUBTOTAL = | | | | | \$990.00 |
| Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (f)). \$0.00 | | | | | |
| TOTAL NATIONAL FEE = | | | | | \$990.00 |
| Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). <input type="checkbox"/> | | | | | \$0.00 |
| TOTAL FEES ENCLOSED = | | | | | \$990.00 |
| | | | | | Amount to be refunded \$ |
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a. ☒ A check in the amount of \$990.00 to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 15-0030. A duplicate copy of this sheet is enclosed.

d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.


NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

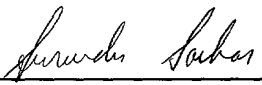
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REGISTRATION NUMBER

6-22-01

DATE

09/857210

JC18 Rec'd PCT/PTO 2 2 JUN 2001

209442US-0PCT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF: :
KARSTEN REIHS ET AL : ATTN: APPLICATION DIVISION
SERIAL NO: NEW U.S. PCT APPLN :
(BASED ON PCT/EP99/10112)
FILED: HEREWITH :
FOR: METHOD FOR PRODUCING AN
ULTRAPHOBIC SURFACE BY
SANDBLASTING

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS
WASHINGTON, D.C. 20231

SIR:

Prior to examination on the merits, please amend the above-identified application as follows.

IN THE CLAIMS

Please cancel Claims 1-12.

Please add new Claims 13-31.

13. (New) A method for producing an ultraphobic surface on metal, glass, ceramic or plastic or a composite of metal and plastic as support material, comprising intensively roughening the support material with a fluid jet containing solid blasting agents over a long

period, the blasting agent having a particle size of $< 200 \mu\text{m}$, optionally coating with an adhesion promoter layer and then providing a hydrophobic coating.

14. (New) The method according to claim 13, wherein the coating is an oleophobic coating.

15. (New) The method according to claim 13, wherein the blasting agent has a particle size of $< 130 \mu\text{m}$.

16. (New) The method according to claim 13, wherein the blasting agent is a metal oxide.

17. (New) The method according to claim 13, wherein the blasting agent is corundum.

18. (New) The method according to claim 13, wherein the blasting agent is crude corundum with sharp-edged particles.

19. (New) The method according to claim 13, wherein the support material is roughened using a fluid jet at a blasting pressure of from 3 to 7 bar and at a distance from the die head to the surface of from 1 to 3 cm.

20. (New) The method according to claim 13, wherein the treatment time of the roughening is from about 0.1 to 10 min/cm².

21. (New) The method according to claim 13, wherein, after the roughening, the surface is coated with a thin layer of noble metal as adhesion promoter layer.

22. (New) The method according to claim 13, wherein, after the roughening, the surface is coated with a thin layer of gold as adhesion promoter layer.

23. (New) The method according to claim 13, wherein, after the roughening, the surface is coated with a thin layer of noble metal as adhesion promoter layer by precipitation of a 10 to 100 nm thick layer.

24. (New) The ultraphobic surface obtained by a method according to claim 13.

25. (New) The material or construction material having an ultraphobic surface obtained by a method according to claim 13.

26. (New) The method of reducing friction comprising lining vehicle bodies, aircraft fuselages or hulls of ships with an ultraphobic surface obtained by a method according to claim 13.

27. (New) The method to produce self cleaning ultraphobic surfaces comprising coating building structures, roofs, windows, ceramic construction material with ultraphobic surfaces obtained according to claim 13.

28. (New) The method for rust protection comprising coating metal objects with an ultraphobic surface obtained by a method according to claim 13.

29. (New) The method to produce a self-cleaning ultraphobic surface comprising topcoating transparent sheets with an ultraphobic surface obtained by a method according to claim 13.

30. (New) The method to produce a self-cleaning ultraphobic surface comprising topcoating transparent glass and plastic sheets with an ultraphobic surface obtained by a method according to claim 13.

31. (New) The method to produce a self-cleaning ultraphobic surface comprising topcoating transparent sheets for solar cells, vehicles or greenhouses with an ultraphobic surface obtained by a method according to claim 13.

REMARKS

Claims 13-31 are active in the present application. New Claims 13-31 are supported by the original Claims 1-12. No new matter is added. An action on the merits and allowance of claims is solicited.

Respectfully submitted,

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IN THE CLAIMS

--Claims 1-12 (Cancelled).

Claims 13-31 (New).--

Method for producing an ultraphobic surface by sandblasting

The present invention relates to a method for producing an ultraphobic surface on metal, glass, ceramic or plastic or a composite of metal and plastic as support material, and to the surface obtained thereby and its use described. In the method, the surface of the support material is roughened with a fluid jet containing solid blasting agents, optionally coated with an adhesion promoter layer and then provided with a hydrophobic coating.

10 Ultraphobic surfaces are characterized by the fact that the contact angle of a drop of liquid, usually water, on the surface is significantly more than 90° and that the roll-off angle does not exceed 10° . Ultraphobic surfaces having a contact angle of $> 150^\circ$ and the abovementioned roll-off angle have a very great technical advantage because, for example, they are not wettable with water or with oil, and soil particles
15 adhere to these surfaces only very poorly and these surfaces are self-cleaning. Here, self-cleaning means the ability of the surface to readily give up soil or dust particles adhering to the surface to liquids which flow over the surface.

There has therefore been no lack of attempts to provide such ultraphobic surfaces.
20 For example, EP 476 510 A1 discloses a method of producing an ultraphobic surface in which a metal oxide film is applied to a glass surface and is then etched using an Ar plasma. However, the surfaces produced using this method have the disadvantage that the contact angle of a drop on the surface is less than 150° .

25 US 5 693 236 also discloses a plurality of methods for producing ultraphobic surfaces, in which zinc oxide microneedles are applied to a surface using a binder and are then partially uncovered in various ways (e.g. by plasma treatment). The surface structured in this way is then coated with a water-repelling composition. However, surfaces structured in this way likewise only have contact angles of up to
30 about 150° .

The object is therefore to provide ultraphobic surfaces, and a method for their production, which have a contact angle of $\geq 150^\circ$, and a roll-off angle of preferably $\leq 10^\circ$.

- 5 In this context, the roll-off angle is the angle of inclination of a fundamentally planar but structured surface toward the horizontal at which a stationary drop of water of volume $10 \mu\text{l}$ is moved as a result of the gravitational force when the surface is inclined.
- 10 The object is achieved according to the invention by the provision of a method, which is the subject-matter of the invention, for producing an ultraphobic surface on metal, glass, ceramic or plastic or a composite of metal and plastic as support material, characterized in that the surface of the support material is intensively roughened with a fluid jet containing solid blasting agents over a relatively long
- 15 period, the blasting agent having a particle size of $< 200 \mu\text{m}$, optionally coated with an adhesion promoter layer and then provided with a hydrophobic, in particular an oleophobic, coating.

- For the purposes of the invention, the substrate which may be used is any plastic, any
- 20 metal, and a composite of metal and plastic. Further substrates (support material) which may be used are ceramic or any materials provided with a ceramic coating, stone-like surfaces, and glass. The substrate can have any desired shape.

- The fluid jet can be formed by any liquids, in particular water or any gases, in
- 25 particular air.

- The solid blasting agent used as additive to the fluid jet may be any granular substance of high hardness which is known to the person skilled in the art. However, the blasting agent preferably has an average particle size of $< 130 \mu\text{m}$.

- 30 The particle size of the blasting agent is preferably at least $2 \mu\text{m}$, particularly preferably at least $5 \mu\text{m}$, very particularly preferably at least $20 \mu\text{m}$.

The structures in the surface of the support material produced by sandblasting have depressions in the order of magnitude of from 2 μm to 500 μm , in particular from 5 μm to 200 μm .

- 5 Surprisingly, the effect of the ultraphobic properties of the treated surfaces is codetermined by the partial incorporation of the blasting agent into the surface of the support material.

- 10 The blasting agent is likewise preferably a metal oxide powder, in particular corundum, very particularly preferably a crude, i.e. unused, corundum with sharp-edged particles.

- 15 The substrate is preferably uniformly roughened using a blasting device which produces a fluid jet and in which fluid and blasting agent are mixed by guiding a jet nozzle over the substrate surface in a grid pattern.

- 20 The blasting pressure is preferably 3 to 7 bar and the distance of the jet nozzle from the substrate surface is 1 to 3 cm for a nozzle diameter of e.g. 1 to 2 mm. The treatment time is in this case, in particular, about 0.1 to 10 min for an area of 1 cm^2 .

After the sandblasting, the surfaces thus obtained are provided with a hydrophobic or, in particular, oleophobic coating.

- 25 For the purposes of the invention, a hydrophobic material is a material which, on a level unstructured surface, has a contact angle based on water of more than 90°.

For the purposes of the invention, oleophobic material is a material which, on a level unstructured surface, has a contact angle based on long-chain n-alkanes, such as n-decane, of more than 90°.

- 30 The ultraphobic surface preferably has a coating with a hydrophobic phobicization auxiliary, in particular an anionic, cationic, amphoteric or nonionic, surface-active

compound. Monomeric or polymeric compounds containing a functional group which produces adhesion promotion to the substrate and has a hydrophobic radical are suitable. Suitable hydrophobic radicals are alkyl radicals, fluorinated alkyl radicals or siloxane groups.

5

Compounds to be regarded as phobicization auxiliaries are surface-active compounds of any molar mass. These compounds are preferably cationic, anionic, amphoteric or nonionic surface-active compounds, as listed, for example, in the directory "Surfactants Europa, A Dictionary of Surface Active Agents available in Europe,"
10 edited by Gordon L. Hollis, Royal Society of Chemistry, Cambridge, 1995.

Examples of anionic phobicization auxiliaries are: alkylsulfates, ether sulfates, ether carboxylates, phosphate esters, sulfosuccinate, sulfosuccinate amides, paraffinsulfonates, olefinsulfonates, sarcosinates, isothionates, taurates and lignin-
15 based compounds.

Examples of cationic phobicization auxiliaries are quaternary alkylammonium compounds and imidazoles

20 Amphoteric phobicization auxiliaries are, for example, betaines, glycines, propionates and imidazoles.

Examples of nonionic phobicization auxiliaries are: alkoxylates, alkylamides, esters, amine oxides and alkyl polyglycosides. Also suitable are: reaction products of
25 alkylene oxides with alkylatable compounds, such as, for example, fatty alcohols, fatty amines, fatty acids, phenols, alkylphenols, arylalkylphenols, such as styrene/phenol condensates, carboxamides and resin acids.

In the case of the monomolecular phobicization auxiliaries, preference is given to
30 those in which 1 to 100%, particularly preferably 60 to 95%, of the hydrogen atoms have been substituted by fluorine atoms. Examples which may be mentioned are perfluorinated alkylsulfate, perfluorinated alkylsulfonates, perfluorinated

alkylphosphonates, perfluorinated alkylphosphinates and perfluorinated carboxylic acids.

As polymeric phobicization auxiliaries for the hydrophobic coating or as polymeric hydrophobic material for the surface, preference is given to using compounds with a molar mass M_w of > 500 to 1,000,000, preferably 1000 to 500,000 and particularly preferably 1500 to 20,000. These polymeric phobicization auxiliaries can be nonionic, anionic, cationic or amphoteric compounds. The polymeric phobicization auxiliaries can contain groups which effect adhesion promotion to the substrate and/or contain groups which are self-crosslinking or can be crosslinked using an external curing agent. In addition, these polymeric phobicization auxiliaries may be homo- and copolymers, graft polymers and graft copolymers, and random copolymers.

The polymeric phobicization auxiliaries preferably contain alkyl groups,

perfluorinated alkyl groups or siloxane groups, (e.g. $\begin{array}{c} \text{R} \quad \text{R} \\ | \quad | \\ \text{---Si---O---Si---} \\ | \quad | \\ \text{R} \quad \text{R} \end{array}$ units where R = $\text{C}_1\text{-C}_4\text{-alkyl}$, preferably methyl).

Particularly preferred polymeric phobicization auxiliaries are those of the type AB, BAB and ABC block polymers. In the AB or BAB block polymers, the A segment is a hydrophilic homopolymer or copolymer, and the B block is a hydrophobic homopolymer or copolymer or a salt thereof.

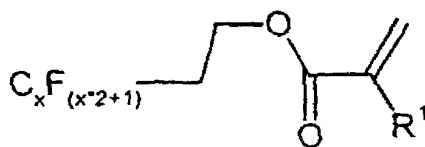
Particular preference is also given to anionic, polymeric phobicization auxiliaries, in particular condensation products of aromatic sulfonic acids with formaldehyde and alkylnaphthalenesulfonic acids or of formaldehyde, naphthalènesulfonic acids and/or benzene sulfonic acids, condensation products of optionally substituted phenol with formaldehyde and sodium bisulfite.

Also preferred are condensation products obtainable by reacting naphthols with alkanols, adding alkylene oxide and at least partially converting the terminal

hydroxyl groups into sulfo groups or monoesters of maleic acid and phthalic acid or succinic acid.

In another preferred embodiment, the phobicization auxiliary is [lacuna] from the group of sulfosuccinates and alkylbenzenesulfonates. Also preferred are sulfated, alkoxyated fatty acids or salts thereof. Alkoxyated fatty acid alcohols means, in particular, those C₆-C₂₂-fatty acid alcohols which are saturated or unsaturated and have 5 to 120, 6 to 60, very particularly preferably 7 to 30, ethylene oxide units, in particular stearyl alcohols. The sulfated alkoxyated fatty acid alcohols are preferably in the form of a salt, in particular an alkali metal or amine salt, preferably diethylamine salt.

Hydrophobic monomers used for the preparation of the polymeric phobicization auxiliaries are compounds of the formula



where x is a natural number from 6 to 12 and

R¹ is hydrogen or methyl, stearyl methacrylate or behenyl methacrylate.

Monomers used for introducing the group promoting adhesion to the substrate are, for example, vinylphosphonic acid, mono(hydroxyethyl methacrylate) phosphate, vinylphenylphosphonic acid, trimethoxyvinylsilane, trimethoxysilylpropyl methacrylate, vinylsilatrane, diethylaminoethyl methacrylate, acrylic acid, methacrylic acid, itaconic anhydride or maleic anhydride.

Monomers used for introducing a self-crosslinking group are, for example, trimethoxysilylpropyl methacrylate or trimethoxyvinylsilane (silane-functional).

Special functional monomers are used to permit crosslinking of the polymer layer.

The acetoacetate group is crosslinkable with di- or polyamines, di- or polyisocyanates or di- or polyacrylates (Michael addition). They are introduced via the monomer methacryloyloxyethyl acetoacetate.

- 5 The epoxy group is crosslinkable with amines or anhydrides. Its introduction is possible via the monomer glycidyl methacrylate.

- The isocyanate group is crosslinkable with di- or polyacetoacetates, di- or polyols, di- or polyamines or compounds containing at least two azomethine groups. Their
10 introduction is possible via α,α -dimethyl-3-isopropenyl-benzyl isocyanate or isocyanatoethyl methacrylate.

- The hydroxyl group is crosslinkable with di- or polyisocyanates, melamine resins or urea resins. It can be introduced via hydroxypropyl methacrylate, hydroxypropyl
15 methacrylate, hydroxybutyl methacrylate, hydroxyethyl methacrylate or hydroxyethyl acrylate.

- The anhydride group is crosslinkable with di- or polyols or di- or polyamines. Its introduction is possible using itaconic anhydride or maleic anhydride.

20

For the crosslinking, it is also possible to use two polymeric phobicization auxiliaries in a mixture or in a two-coat application which have groups which react with one another.

- 25 In addition, the isocyanate-, epoxy- or anhydride-functional polymers can be reacted with hydroxyethyl acrylate or methacrylate. The resulting (meth)acrylate-functional resins are free-radically (photochemically, by electron beams or free-radical initiators) crosslinkable.

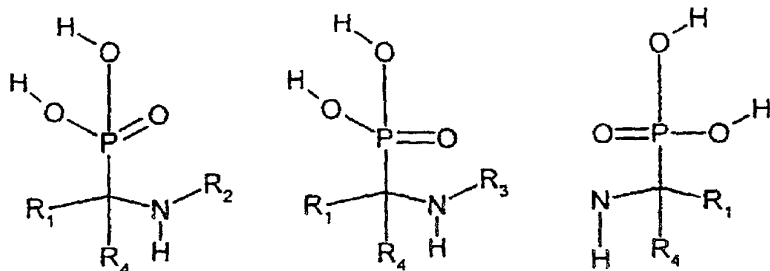
- 30 During the preparation, 0 - 50% by weight of monomers which are neither adhesion-promoting, hydrophobic or crosslinking can be added to the polymeric phobicization

auxiliaries. Examples thereof are styrene, methyl methacrylate, butyl acrylate, butyl methacrylate, ethylhexyl methacrylate, methyl acrylate or ethyl acrylate.

5 The polymeric phobicization auxiliaries are preferably prepared by free-radical polymerization in the presence of an initiator (peroxy or azo compound) in a solvent. For polymeric phobicization auxiliaries which contain perfluoroalkyl groups, preference is given to ketones, such as, for example, butanone, methyl isobutyl ketone or cyclohexanone.

10 To improve the adhesion of the hydrophobic or oleophobic coating to the sandblasted substrate, it may be advantageous to firstly coat the surface of the sandblasted substrate with an adhesion promoter layer. Therefore, an adhesion promoter layer is optionally applied between the surface and the hydrophobic or oleophobic coating. In principle, the adhesion promoter may be any substance known to the person skilled in
15 the art which increases the bonding between the surface and the respective hydrophobic or oleophobic coating. Preferred adhesion promoters, e.g. for thiols as a hydrophobic coating, are layers of noble metals, e.g. of Au, Pt or Ag or those of GaAs, in particular of gold. The thickness of the adhesion promoter layer is preferably 10 to 100 nm.

20 Preferred adhesion promoters for functional polymeric phobicization auxiliaries are vinylphosphonic acid, mono(hydroxyethyl methacrylate) phosphate, allylphosphonic acid, allylamine, maleic anhydride, acrylic acid, allyl sulfide, trimethoxyvinylsilane, trimethoxysilylpropyl methacrylate, trimethoxysilylpropyl mercaptan,
25 glycididloxypropoxypropyltrimethoxysilane, diethylaminoethyl methacrylate and aminophosphonic acids. Preference is given to aminophosphonic acids of the formulae



where

R₁ and R₄ are hydrogen, C₁-C₂₂-alkyl or C₆-C₁₀-aryl, preferably hydrogen or phenyl,

5

R₃ is C₂-C₂₂-alkylene or C₅-C₂₀-cycloalkylene and

R₂ is hydrogen or C₁-C₂₂-alkyl.

10 Using the method according to the invention it is possible to prepare ultraphobic surfaces for which the contact angle of a drop on the surface is $\geq 155^\circ$. The invention therefore also provides the ultraphobic surfaces obtained by the method according to the invention.

15 These ultraphobic surfaces have the advantage, inter alia, that they are self-cleaning, self-cleaning taking place when the surface is exposed from time to time to rain or moving water. As a result of the ultraphobic surface, the drops of water roll off the surface, and soil particles, which adhere only very poorly to the surface, settle on the surface of the drops which are rolling off and are thus removed from the ultraphobic surface. This self-cleaning is effective not only upon contact with water but also with oil.

20 There are a large number of industrial use possibilities for the surface produced by the method according to the invention. Also claimed, therefore, are the following uses of the ultraphobic surfaces produced by the method according to the invention:

25

Hulls of ships can be coated with the ultraphobic surface produced by the method according to the invention in order to reduce their resistant to friction.

As a result of the fact that water does not adhere to the ultraphobic surface produced
5 by the method according to the invention, it is suitable as a rust inhibitor for base metals of any type.

In addition, sanitary installations, in particular toilet bowls, can be provided with the ultraphobic surface produced by the method according to the invention in order to
10 reduce their susceptibility to soiling.

A further use of the ultraphobic surface is the coating of surfaces to which water must not adhere in order to avoid icing over. Examples which may be mentioned here are the surfaces of heat exchangers, e.g. in refrigerators, or the surfaces of aircraft.
15

The surfaces produced by the method according to the invention are also suitable for fixing to house façades, roofs, monuments in order to render these self-cleaning.

The ultraphobic surfaces produced by the method according to the invention are also
20 suitable, in particular, for the coating of moldings which are transparent. In particular, these may be transparent glazings of buildings, vehicles, solar collectors. For this, a thin layer of the ultraphobic surface according to the invention is applied to the molding by vapor deposition.

25 The invention also provides a material or construction material having an ultraphobic surface according to the invention.

The invention further provides for the use of the ultraphobic surface according to the invention for the friction-reducing lining of vehicle bodies, aircraft fuselages or hulls.
30

The invention also provides for the use of the ultraphobic surface according to the invention as self-cleaning coating or paneling of building structures, roofs, windows, ceramic construction material, e.g. for sanitary installations, household appliances.

- 5 The invention further provides for the use of the ultraphobic surface according to the invention as an antirust coating of metal objects.

The method according to the invention is illustrated below by reference to examples.

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Examples

Example 1

- 5 An extruded polymethyl methacrylate sheet with an area of $10 \times 10 \text{ mm}^2$ and a thickness of 3 mm was sandblasted using a 3-chamber blasting device (model name: Kermo 3) from Renfert GmbH, D-78245 Hilzingen. The blasting agent used was corundum from Renfert. The fluid used for the fluid jet was air. The blasting agent was unused and had an Al_2O_3 content of $< 99.5\%$ by weight and an average particle
10 size of $125 \text{ }\mu\text{m}$. The jet nozzle used was a round nozzle with a diameter of 1.2 mm from Renfert. The polymer sheet was sandblasted with a blasting pressure of 5 bar, the distance of the round nozzle from the polymer surface being 1.5 cm and the jet nozzle being guided over the sheet in a grid pattern. The sheet was treated for 1 minute. The substrate then had irregularly distributed indentations and raised areas 50
15 to $200 \text{ }\mu\text{m}$ in size.

- The substrate treated in this way was coated with an approximately 50 nm-thick gold layer by atomization. This coating method corresponds to the method which is also customary for the preparation in electron microscopy and is described by Klaus
20 Wetzig, Dietrich Schulze, "In situ Scanning Electron Microscopy in Material Research", page 36-40, Akademie Verlag, Berlin 1995. This literature reference is hereby incorporated as reference and is accordingly to be regarded as part of the disclosure.

- 25 Finally, the gold layer of the sample was coated with a few drops of a solution of n-perfluorooctanethiol in α, α, α -trifluorotoluene (1 g/l) at room temperature in a sealed vessel, then rinsed with α, α, α -trifluorotoluene and dried.

- The surface has a static contact angle for water of $> 160^\circ$. A drop of water of volume
30 $10 \text{ }\mu\text{l}$ rolls off if the surface is inclined by $< 3^\circ$.

Example 2

5 A titanium sheet $30 \times 30 \text{ mm}^2$ in size and 2 mm in thickness was roughened as in Example 1 using a fluid jet containing corundum, although here a blasting material with an average particle size of $90 \mu\text{m}$ was used. These roughened sheets are cleaned in ethanol and dried in air. They are then immersed in a 0.1% strength solution of phosphate-functional, perfluorinated binding agent (solvent MIBK) for 24 h and then briefly swirled in pure MIBK and then dried at 120°C for 20 h.

10 The binder is prepared as follows:

I. Phosphonate-functional perfluorinated binder

15 70 g of perfluorinated acrylate (Zonyl TA-N®), 25 g of methacryloyloxyethyl acetoacetate, 5 g of a 50% strength aqueous solution of vinylphosphonic acid, 100 g of methyl iso-butyl ketone, 1 g of azobisisobutyronitrile and 5 g of an ethoxylated nonylphenol (with 20 ethylene oxide units) are mixed, and the solution is allowed to run into a flask heated to 90°C in 2 hours. 3 ml of triethylamine are added and the mixture is then stirred for 6 hours.

20

The surface has a static contact angle for water of $> 150^\circ$. A drop of water of volume $10 \mu\text{l}$ rolls off if the surface is inclined by $< 10^\circ$.

Example 3

25

A titanium sheet $30 \times 30 \text{ mm}^2$ in size and 2 mm in thickness was roughened as in Example 1 using a fluid jet containing corundum, although here a blasting material with an average particle size of $90 \mu\text{m}$ was used. These roughened sheets are cleaned in ethanol and dried in air. They are then immersed in a 0.1% strength solution of silane-functional perfluorinated binder (solvent MIBK) for 24 h and then briefly swirled in pure MIBK and then dried at 120°C for 20 h.

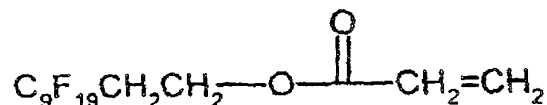
30

The binder is prepared as follows:

The mixture of 70 g of perfluorinated acrylate, 30 g of trimethoxysilylpropyl methacrylate, 1 g of azobisisobutyronitrile and 100 g of methyl butyl ketone is heated
 5 at 65°C for 16 h. Prior to application, 0.1% by weight, based on the polymer mass, of dodecylbenzenesulfonic acid is also added to this solution.

II. Silane-functional perfluorinated binder

10 The perfluorinated acrylate is an acrylate containing a fluorinated C₆-C₁₂-radical and corresponding to an average structural formula:



The surface has a static contact angle for water of > 150°. A drop of water of volume
 15 10 µl rolls off if the surface is inclined by < 10°.

Example 4

A titanium sheet 30 × 30 mm² in size and 2 mm in thickness was roughened as in
 Example 1 using a fluid jet containing corundum, although here a blasting material
 20 with an average particle size of 90 µm was used. These roughened sheets are cleaned
 in ethanol and dried in air. They are then immersed in a 0.1% strength solution of
 aminophosphonic acid in butanol for 24 h and then briefly swirled in pure MIBK and
 then dried at 120°C for 1 h. To the adhesion promoter layer applied in this way is
 applied a 0.1% strength solution of epoxy-functional perfluorinated binder (solvent
 25 MIBK) by homogenous spraying with an atomizer attachment for measuring
 cylinders with ground-glass joints (Görres; initial pressure 2 bar of N₂) from a
 distance of about 20 cm. The sheet is then dried at 120°C for 20 h.

The aminophosphonic acid is prepared as follows:

III. Aminophosphonic acid dissolved in butanol

The mixture of 11.6 g of 1,6-diaminohexane, 212 g of benzaldehyde, 500 g of butanol and 1 g of phosphorous acid is boiled for 8 hours at the water separator for
5 light solvents. 164 g of phosphorous acid are added, and the mixture is heated for 2 hours at 120°C.

The binder is prepared as follows:

10 IV. Epoxy-functional perfluorinated binder

The mixture of 60 g of perfluorinated acrylate, 20 g of styrene, 20 g of glycidyl methacrylate. 1 g of azobisisobutyronitrile and 100 g of butanone is heated at 65°C
15 for 16 hours.

The surface has a static contact angle for water of $> 150^\circ$. A drop of water volume 10 μl rolls off if the surface is inclined by $< 10^\circ$.

Example 5

20

In this example a 2 mm-thick titanium sheet was roughened exactly as in Example 1 using a fluid jet containing corundum.

The sheet treated in this way was immersed in a 1% strength by weight solution of
25 Fluowet PL80 (mixture of perfluorinated phosphanates and phosphinates) from Clariant for 5 hours at pH 7 and then rinsed with water and dried at 60°C.

The surface has a static contact angle for water of $> 160^\circ$. A drop of water of volume 10 μl rolls off if the surface is inclined by $< 3^\circ$.

Example 6

In this example a 2 mm-thick V4A stainless steel sheet was roughened exactly as in Example 1 using a fluid jet containing corundum.

5

The sheet treated in this way was immersed into a 1% strength by weight solution of Fluowet PL80 from Clariant for 5 hours at pH 7 and then rinsed with water and dried at 60°C.

- 10 The surface has a static contact angle for water of $> 160^\circ$. A drop of water of volume 10 μl rolls off if the surface is inclined by $< 5^\circ$.

Example 7

- 15 In this example a 2 mm-thick titanium sheet was roughened as exactly as in Example 1 with a fluid jet containing corundum.

The sheet treated in this way was immersed in a 1% strength by weight solution of Hoe S2746 (mixture of perfluorinated phosphonates and phosphinates) from Clariant

- 20 for 5 hours at pH 7 and then rinsed with water and dried at 60°C.

The surface has a static contact angle for water of $> 160^\circ$. A water droplet of volume 10 μl rolls off if the surface is inclined by $< 5^\circ$.

- 25 **Example 8**

In this example a 2 mm-thick titanium sheet was treated exactly as in Example 1. In this example too the surface has a static contact angle for water of $> 160^\circ$. A drop of water of volume 10 μl rolls off if the surface is inclined by $< 3^\circ$.

30

Patent claims

1. Method for producing an ultraphobic surface on metal, glass, ceramic or plastic or a composite of metal and plastic as support material, characterized
5 in that the surface of the support material is intensively roughened with a fluid jet containing solid blasting agents over a relatively long period, the blasting agent having a particle size of $< 200 \mu\text{m}$, optionally coated with an adhesion promoter layer and then provided with a hydrophobic, in particular an oleophobic, coating.
10
2. Method according to Claim 1, characterized in that the blasting agent has a particle size of $< 130 \mu\text{m}$.
3. Method according to one of Claims 1 or 2, characterized in that the blasting
15 agent is a metal oxide, preferably corundum, particularly preferably crude corundum with sharp-edged particles.
4. Method according to one of Claims 1 to 3, characterized in that the support
20 material is roughened using a fluid jet at a blasting pressure of from 3 to 7 bar and at a distance from the die head to the surface of from 1 to 3 cm.
5. Method according to Claim 4, characterized in that the treatment time of the roughening is from about 0.1 to 10 min/cm^2 .
- 25 6. Method according to one of Claims 1 to 5, characterized in that, after the roughening, the surface is coated with a thin layer of noble metal as adhesion promoter layer, preferably a gold layer, in particular by precipitation of a 10 to 100 nm-thick layer.
- 30 7. Ultraphobic surface obtained by a method according to one of Claims 1 to 6.

8. Material or construction material having an ultraphobic surface according to Claim 7.
- 5 9. Use of the ultraphobic surface according to Claim 7 for the friction-reducing lining of vehicle bodies, aircraft fuselages or hulls of ships.
- 10 10. Use of the ultraphobic surface according to Claim 7 as self-cleaning coating or paneling of building structures, roofs, windows, ceramic construction material, e.g. for sanitary installations, household appliances.
- 10 11. Use of the ultraphobic surface according to Claim 7 as an antirust coating of metal objects.
- 15 12. Use of the ultraphobic surface according to Claim 7 as topcoat of transparent sheets, in particular glass and plastic sheets, in particular for solar cells, vehicles or greenhouses.

Abstract

The invention relates to a method for producing an ultraphobic surface on metal, glass, ceramics, or plastic or on a composite which is comprised of metal and plastic and which is used as supporting material. The invention also relates to the surface obtained by using said method, and to the use of the surface. According to the method, the surface of the supporting materials is roughened using a fluid jet containing solid blasting abrasives, is optionally coated with a bonding agent layer, and is subsequently provided with a hydrophobic coating.

PCT/EP99/10112

Declaration and Power of Attorney For Patent Application

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Method for producing an ultraphobic
surface by sand blasting

deren Beschreibung
(zutreffendes ankreuzen)

☐ hier beigefügt ist.
☐ am _____ unter der

Anmeldungsseriennummer _____

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the specification of which

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☐ was filed on _____ as

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I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

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(Frühere ausländische Anmeldungen)

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| (Number) | (Country) |
| (Number) | (Land) |

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Priority Not Claimed
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| 24.12.1998 | <input type="checkbox"/> |
| (Day/Month/Year Filed) | |
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